# Reactions of Fluorocyclopentene Derivatives with Nucleophilic Agents

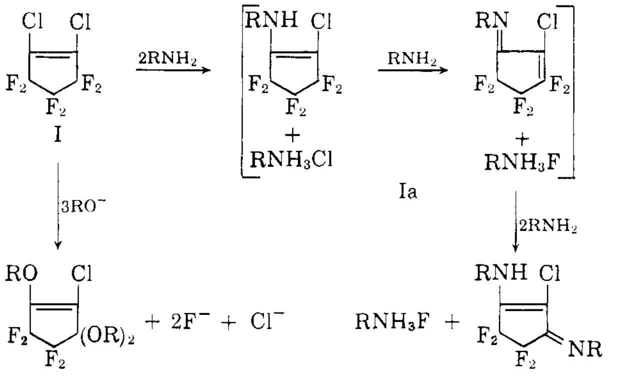
T. MILL, J. O. RODIN, R. M. SILVERSTEIN, AND C. WOOLF[1]

*Stanford Research Institute, Menlo Park, California, and General Chemical Division, Allied Chemical Corporation, Morristown, New Jersey*

*Received August 16, 1962*

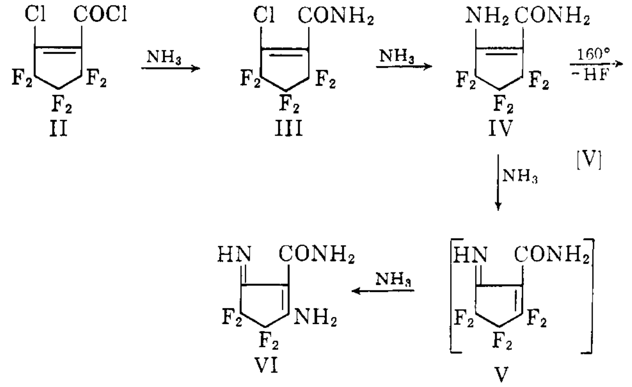
The fluorinated olefin, 1-chloro-2-carboxamidohexafluorocyclopentene-1 (III), undergoes selective substitution by one or two molecules of ammonia or aniline in contrast to the unselective substitution by aniline in 1,2-dichlorohexafluorocyclopentene-1 (I). The carboxamide group serves to facilitate nucleophilic addition to the ring and to retard subsequent dehydrofluorination, probably by hydrogen bonding. Hydride ion addition to III leads to partial or complete reduction of the ring followed by reduction of the carboxamide group.

Nucleophilic addition to fluoroölefins has been the subject of several studies during the last ten years.[2] Recently Parker has examined the reaction of amines with the cyclic fluoroölefin, 1,2-dichlorohexafluorocyclopentene-1 (I).[3] He postulated an addition-elimination sequence involving 1,4-dehydrofluorination to account for the observation that primary, but not secondary amines add twice to the olefin, giving only the 1,3-diamine substitution products.



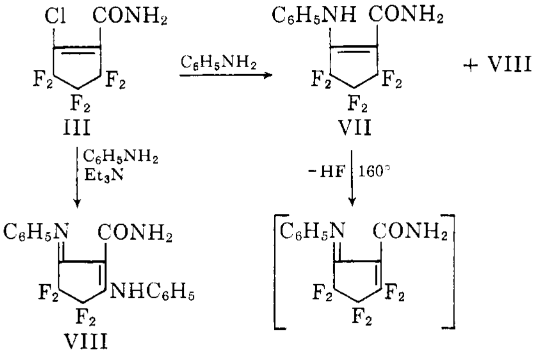
With excess alkoxide ion, addition-elimination to dichlorohexafluorocyclopentene, followed by allylic substitution, leads to the formation of 1,3,3-trialkoxy-2-chlorotetrafluorocyclopentene. Analogous reactions have been observed between acyclic fluoroölefins and alkoxide ions.[4] We have examined the reactions of several nucleophilic species with 1-chloro-2-carboxamidohexafluorocyclopentene-1 (III),[5] and have obtained results which relate to the reaction sequences outlined above.

**Reactions with Amines.**—Careful treatment of 1-chloro-2-chloroformylhexafluorocyclopentene-1 (II) with limited amounts of ammonia afforded a series of compounds (III–VI) corresponding to substitution by one to three amino groups in II.



Elemental analyses and infrared and n.m.r. spectra are in accord with structures indicated for III, IV, and VI. Special interest attaches to the observation that alone of the series, IV, melted with decomposition, evolving hydrogen fluoride. Although efforts to isolate the product of this decomposition either from the melt or by treatment of IV with triethylamine gave only colored resin, it seems clear that the initial product must be V, corresponding to 1,4-dehydrofluorination of IV.

When 1-chloro-2-carboxamidohexafluorocyclopentene-1 (III) was treated with a mixture of one equivalent of aniline and one equivalent of triethylamine at 0°, only starting material and 1-phenylamino-2-carboxamido-3-phenyliminotetrafluorocyclopentene-1 (VIII) were isolated. Treatment of III with two equivalents of aniline, however, did afford a modest yield of 1-phenylamino-2-carboxamidohexafluorocyclopentene-1 (VII), plus a major amount of VIII. Like IV, VII evolved hydrogen fluoride on heating at 160°, no product being isolable from the melt.



The fact that both ammonia and aniline will substitute III (with different degrees of selectivity) to give the monoamine products, whereas I is reported to undergo disubstitution exclusively,[3] prompted us to

---

[1] General Chemical Division, Allied Chemical Corporation, Morristown, N. J.

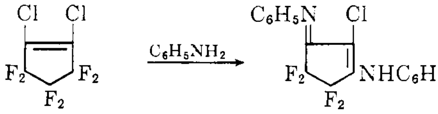
[2] D. D. Coffmann, M. S. Raasch, G. W. Rigby, P. L. Barrick, and W. E. Hanford, *J. Org. Chem.*, **14**, 747 (1949); J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646, 4480 (1950); N. N. Yavorenko, M. A. Raksha, V. N. Shemanina, and A. S. Vasileva, *Zh. Obshch. Khim.*, **27**, 2246 (1957); I. L. Knunyants, L. S. German, and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (**2**), 221 (1960); W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

[3] C. O. Parker, *ibid.*, **81**, 2183 (1959).

[4] I. L. Knunyants, B. L. Dyatkin, L. S. German, and E. P. Mochalina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (**2**), 211 (1960) (English transl.).

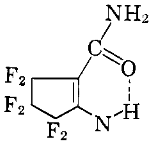
[5] This nomenclature form has been adopted in order to retain the 1–3 numbering system for disubstitution products described here and thus to emphasize the structural features common to compounds of this and earlier work (ref. 3).

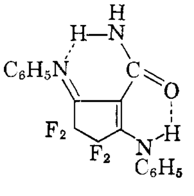
examine the reaction of 1,2-dichlorohexafluorocyclopentene-1 (I) with aniline. The reaction was sluggish at room temperature and, on warming the mixture in tetrahydrofuran, only the disubstitution product, 1-phenylamino-2-chloro-3-phenyliminotetrafluorocyclopentene-1 (IX), was found. Repetition of the experiment, using a 10:1 ratio of 1,2-dichlorohexafluorocyclopentene to aniline, gave, after four months at room temperature, only starting materials and IX.


I IX

These experimental data suggest that aniline displaces chlorine in III 1000–10,000 times faster than in I. The greater conjugative capacity of the carboxamide group compared to chlorine is responsible for this rate effect and probably accounts for selectivity exhibited by III with respect to mono- and disubstitution. Hydrogen bonding in III (see below) might serve to enhance this selectivity by depressing the rate of dehydrofluorination of VII relative to that of intermediate Ia, possibly by as large a factor as 5000.

**Hydrogen Bonding.**—The proton n.m.r. spectra of VII and VIII (Table I) showed amino-hydrogen peaks shifted downfield from the same proton peak in the spectrum of IX ($\tau$ = 0.50, −1.48, 3.48, respectively). The spectrum of VII showed a single amide proton peak, but the spectrum of VIII showed two amide proton peaks ($\tau$ = 3.83, 0.90). Both the lowfield amino and amide proton peaks of VIII were unshifted on fourfold dilution; the upfield amide peak however did display slight upfield shift on dilution. These spectral differences and changes suggest cyclic hydrogen bonded structures, VIIa and VIIIa.[6]


VIIa


VIIIa

Additional indirect evidence for the presence of hydrogen bonds in diamine structures VI and VIII was obtained from the $F^{19}$ n.m.r. spectra of VI, VIII and IX. (Table II). Compound IX exhibits only a single peak indicating rapid proton exchange, either between nitrogens or between carbon and nitrogen, making the geminate pairs of fluorines equivalent.[7]

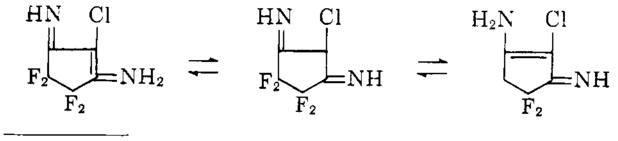


TABLE I

INFRARED[a] AND PROTON N.M.R.[b] SPECTRA

| Compound | Infrared band $\mu$ | N.m.r. band $\tau$ | Area | Multiplicity | Assignment |
|---|---|---|---|---|---|
| VII | 2.83, 2.89 | 4.03 | 2 | Broad | $CONH_2$ |
| | | 2.68 | 5.2 | Complex | Aromatic |
| | 3.05 | −0.50 | 1 | Broad | $C_6H_5NH$ |
| VIII | 3.05 | 3.83 | 1 | Broad | CONH |
| | | 2.95 | 10 | Complex | Aromatic |
| | 2.87 | 0.90 | 1 | Broad | CONH |
| | 3.0–3.1 | −1.48 | 1 | Broad | $C_6H_5$-N$H$ |
| IX | | 3.48 | 1 | Broad | $C_6H_5NH$ |
| | | 2.83, 2.75 | 10 | Complex | Aromatic |

[a] Spectra obtained on 10% solutions in carbon tetrachloride. [b] Spectra obtained on 10% solutions in deuteriochloroform.

TABLE II

FLUORINE N.M.R. SPECTRA[a]

| Compound | $\phi^9$ (p.p.m.) | Assignment[b] |
|---|---|---|
| III | 131.0 | 4 |
| | 115.2 | 5 |
| | 110.0 | 3 |
| IV | 130.4 | 4 |
| | 125.4 | 5 |
| | 101.2 | 3 |
| VI | 122.9 | 4 |
| | 121.2 | 5 |
| VIII | 113.8 | |
| IX | 112.6 | |
| X (ether) | 118.5 | |
| | 116.8 | |
| XI (THF)[c] | 116.1 | 4 |
| | 109.3 | 5 |
| XII (THF) | 117.2 | |
| | 115.2 | |

[a] Because of low solubility, some samples were run in ether or tetrahydrofuran instead of trichlorofluoromethane. Quoted $\phi$ values are thus approximate and are not all strictly comparable, one with another; ref. 9. [b] Numbers refer to ring positions of fluorines. In X and XII, the bands arise from vicinal pairs, *cis* or *trans* to substituent in 2 position. [c] Tetrahydrofuran.

The diamine adducts having carboxamide groups (VI, VIII) each displayed two $F^{19}$ n.m.r. peaks. Here exchange must be slowed by the hydrogen bonding, preserving the asymmetry of the rings.

Inspection of the N—H stretching region of the infrared spectra of these compounds (Table I) revealed a reasonable degree of concordance with the n.m.r. spectra.[8]

**Reaction of III with Lithium Aluminum Hydride.**—Hydride ion addition to III was examined by treating III with both limited and excess amounts of lithium aluminum hydride in tetrahydrofuran. Under the former conditions, low yields of two new materials (XI, XII) were isolated and separated by gas chromatography. Both materials were solids, m.p., 139–141° and 141–148°. Each displayed an amide carbonyl band in its infrared spectrum and two equal-area $F^{19}$ n.m.r. bands (Table II.) The reaction of III with an excess of lithium aluminum hydride afforded only one amine, having correct analyses for 1,1,2,3,3-pentahydro-2-aminomethyltetrafluorocyclopentane (X). The $F^{19}$ n.m.r. spectrum of X displayed two equal-area bands, with

---

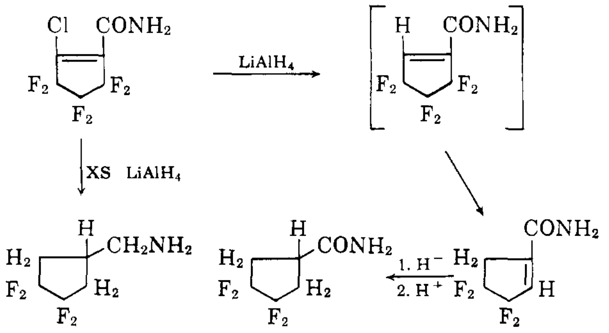
(6) W. G. Schneider and L. W. Reeves, *Ann. N. Y. Acad. Sci.*, **70**, 858 (1958).

(7) C. O. Parker (ref. 3) reports the presence of only one $F^{19}$ n.m.r. band for 1-methylamino-2-chloro-3-methyliminotetrafluorocyclopentene-1 and postulates an intermolecular hydrogen transfer mechanism. Alternatively, the 1,3-bisimino structure can also give rise to equivalent fluorines, providing intramolecular transfer is rapid.

(8) For a discussion of the interpretation of N—H stretching modes relative to position and shape see L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 248–55.

$\phi$ values[9] very similar to those of the higher-melting amide product. We have therefore assigned structure XII to the higher melting amide and XI to the other amide, corresponding respectively to addition of five and three hydrogens to the cyclopentene ring.

We suggest that hydride ion attacks the double bond with substitution of chlorine followed by an S$_N$2′ displacement of fluorine to give XI; a reaction path analogous to that observed for alkoxide ion on I.[10] An unusual feature of the reaction is the rapid addition of hydride to the ring compared with addition to the carboxamide group.[11] Flanking difluoromethylene and carboxamide groups must be responsible for the highly electrophilic character of the double bonds in these compounds.



X XII XI

## Experimental[12]

**Infrared Spectra.**—All infrared spectra were taken on a Beckman Instrument Company IR-5 recording spectrophotometer employing sodium chloride optics.

**N.m.r. Spectra.**—A Varian Associates High Resolution n.m.r. spectrometer was employed for proton spectra at 60 Mc. and at 56.4 Mc. for fluorine spectra.

**1-Chloro-2-carboxamidohexafluorocyclopentene-1 (III).**—An ammoniacal solution of tetrahydrofuran was made up and the concentration of ammonia established by titration. Such a solution (80 ml. of tetrahydrofuran containing 0.04 mole of ammonia) was added dropwise (20 min.) to a solution of 5.46 g. (0.020 mole) of 1-chloro-2-chloroformylhexafluorocyclopentene-1[13] in 20 ml. of dry tetrahydrofuran at 0° with stirring. The suspension was stirred for 5 min. at 0° and the solvent was removed by pumping at 20 mm. The white crystalline residue was triturated with 100 ml., and then 50 ml., of boiling methylene chloride, and the solution was concentrated to a volume of 30 ml. and cooled to 0°. The product was separated by filtration and washed with cold methylene chloride; wt. = 3.4 g. (67% yield); m.p. 116–118°; $\lambda_{\max}^{\text{nujol}}$ 2.95, 3.12, 6.01, 6.07 (sh) $\mu$.

A sample was recrystallized from methylene chloride; m.p. 116–118°.

*Anal.* Calcd. for $C_6H_2NOClF_6$ (253.5): N, 5.52; Cl, 14.0. Found: N, 5.39; Cl, 13.6.

**1-Amino-2-carboxamidohexafluorocyclopentene-1 (IV).**—A solution of 0.0040 mole of ammonia in 7.5 ml. of dry tetrahydrofuran was added dropwise (15 min.) to a stirred solution of 0.51 g. (0.0020 mole) of III in 2 ml. of dry tetrahydrofuran at 0°. The suspension was stirred at 0° for 5 min. and the solvent was removed by pumping at 20-mm. pressure. The white crystalline residue was triturated with boiling ether (3 × 10 ml.). The insoluble material weighed 0.085 g. and contained 0.9% fluoride ion by analysis. The ether solution was concentrated to 2 ml.; petroleum ether (10 ml.) was added and the solution was concentrated to 5 ml. and cooled to 0°. The product was isolated by filtration; wt. = 0.38 g.; m.p. 159–160° with decomposition.

*Anal.* Calcd. for $C_6H_4N_2OF_6$ (234.1): C, 30.8; H, 1.72; N, 11.96. Found: C, 31.0; H, 1.53; N, 12.1.

A 100-mg. sample of IV was placed in a flask equipped with a gas outlet tube leading into an ethereal solution of aniline. The flask was heated with an oil bath at 160° for 1 hr. Gas was evolved and a white precipitate separated from the ether solution and was isolated. The precipitate gave a positive test for fluoride ion (color changed from deep orange to light yellow) when treated with ferric thiocyanate solution,[14] under conditions where chloride ion gave no change.

**1-Amino-2-carboxamido-3-iminotetrafluorocyclopentene-1 (VI).**—Anhydrous ammonia was passed through a solution of 1.7 g. (0.0062 mole) of II in 20 ml. of dry ether for 15 min. while cooling with an ice bath. The suspension was stirred at 25° for 15 min. and filtered. The filtrate was concentrated at 20 mm. pressure and the white crystalline residue was recrystallized from a tetrahydrofuran: petroleum ether solution; wt. = 0.98 g., (75% yield); m.p. 188–189°.

A sample was recrystallized from tetrahydrofuran–petroleum ether; m.p. 189–190°; $\lambda_{\max}^{\text{nujol}}$ 5.96, 6.13 $\mu$.

*Anal.* Calcd. for $C_6H_5N_3OF_4$ (211.1): C, 34.1; H, 2.39; N, 19.9. Found: C, 34.2; H, 2.39; N (Dumas), 19.8, 21.2, 18.5.

The reaction between 1-amino-2-carboxamidohexafluorocyclopentene-1 and excess ammonia gave the same product.

**Reaction of III with Aniline–Triethylamine.**—A solution of 0.186 g. (0.0020 mole) of aniline in 5 ml. of dry tetrahydrofuran was added dropwise (15 min.) to a stirred solution of 0.51 g. (0.0020 mole) of III and 0.20 g. (0.0020 mole) of dry triethylamine in 5 ml. of dry tetrahydrofuran at 0°. The mixture was stirred at 0° for 2 hr. and concentrated at 20-mm. pressure to a crystalline residue which was triturated with 20 ml. of ether. The ether solution was reconcentrated and the residue was triturated with 25 ml. of boiling heptane. The crystals which precipitated upon cooling in ice were separated by filtration and washed with cold heptane; wt. = 0.45 g.; m.p. 115–140°. This sample was sublimed at 0.15-mm. pressure and two fractions were collected: a fraction at 60–100° which proved to be starting material; m.p. 114–117°—and a fraction at 160° (VIII); m.p. 165–166°; light yellow, $\lambda_{\max}^{CCl_4}$ 6.02, 6.18, 6.29, 6.66 $\mu$.

*Anal.* Calcd. for $C_{19}H_{13}N_3OF_4$ (363.3): C, 59.6; H, 3.61; N, 11.6. Found: C, 59.5; H, 3.36; N, 11.81.

**Reaction of III with Two Equivalents of Aniline.**—One gram (4.0 mmoles) of III was added to a solution of 0.72 ml. (8.0 mmole) of aniline in 20 ml. of ether at 0°, stored overnight at 0°, and filtered. The filtrate was evaporated; the residue was triturated with ether, and pentane was added, giving a small amount of crystals. This filtrate was then concentrated to 6 ml. and filtered to give 0.75 g. of yellow solid; m.p. 85–140°. The solid was sublimed at 0.2 mm., giving the following fractions:

1. 40–85°—0.20 g.; m.p. 110–116°; starting material
2. 90°—0.15 g.; m.p. 101–104°; VII
3. 130°—0.05 g.; m.p. 90–95°; VII
4. 160–200°—0.30 g.; m.p. 162–164°; VIII

Fractions 2 and 3 were combined and recrystallized from heptane; white crystals; m.p. 100–103°; gassing at 165°.

*Anal.* Calcd. for $C_{12}H_{18}N_2OF_6$ (310.2): C, 46.5; H, 2.60; N, 9.04. Found: C, 46.8; H, 2.51; N, 8.79.

**1-Phenylamino-2-chloro-3-phenyliminotetrafluorocyclopentene-(IX).**—A solution of 18.4 g. (0.198 mole) of aniline in 50 ml. of dry tetrahydrofuran was added dropwise (1 hr.) to a stirred solution of 27.2 g. (0.11 mole) of 1,2-dichlorohexafluorocyclopentene-1 in 50 ml. of dry tetrahydrofuran at 0°. As there was no evidence of reaction, the solution was brought to reflux. Crystals began to separate after 1.5 hr. and the suspension was refluxed for 20 hr., cooled to 25°, and filtered (wt. of insoluble material = 5.7 g.). The filtrate was concentrated at 20-mm pressure to 28 g. of partially crystalline residue, to which was added a few milliliters of carbon tetrachloride followed by *ca.* 100 ml. of petroleum ether at 25°. The mixture was filtered to give 12 g. of solid. The filtrate was distilled at 15-mm. pressure, and 6 g. of liquid collected at 67° was shown to be aniline by its infrared spectrum.

---

[9] G. V. D. Tiers and G. Filipovich, *J. Phys. Chem.*, **63**, 761 (1959).

[10] Unpublished results of T. Mill.

[11] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 591.

[12] All melting points and boiling points are uncorrected.

[13] Prepared from 1-methoxy-2-chlorohexafluorocyclopentene-1, according to directions supplied by Dr. R. F. Sweeney, General Chemical Division, Allied Chemical Corporation, Morristown, N. J.

[14] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 750.

A sample of the above solid was recrystallized twice from ether–petroleum ether (1:15); yellow crystals: m.p. 127–128°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.94, 6.13, 6.27 μ.

*Anal.* Calcd. for $C_{17}H_{11}N_2ClF_4$ (354.7): C, 57.6; H, 3.12; N, 7.90. Found: C, 57.4; H, 3.06; N, 8.06.

**Reduction of 1-Chloro-2-carboxamidohexafluorocyclopentene-1 (III) with Lithium Aluminum Hydride.**—(a) A solution of 1.27 g. (0.0050 mole) III in 5 ml. of tetrahydrofuran was added to 0.20 g. (0.0053 mole) of lithium aluminum hydride in 10 ml. of tetrahydrofuran held at 5°. The mixture was refluxed 16 hr. under nitrogen. The resultant black suspension was cooled in Dry Ice and decomposed by successive dropwise addition of 0.2 ml. of water, 0.6 ml. of 15 *N* sodium hydroxide solution, and 0.2 ml. of water. The mixture was then centrifuged. The supernatant liquid was boiled to 1 ml. volume and distilled in a 15-mm. tube at 5-mm. pressure.

The distillate was fractionated on a 10-ft. silicone-550 column at 190°. The three principal components were collected at indicated elution times.

1. 8 min.—m.p. 116–117°; wt. = 15 mg. starting material.
2. 16 min.—m.p. 139–141°; wt. = 15 mg. identified as XI by n.m.r.
3. 20 min.—m.p. 141–148°; wt. = 18 mg. identified as XII by n.m.r.

(b) Five grams of III (0.02 mole) was treated with 2.3 g. (0.06 mole) of lithium aluminum hydride in 50 ml. of tetrahydrofuran. After decomposition and centrifugation, the solvent was evaporated, leaving 6 g. of residue which was distilled (100°/140 mm.), giving 1.2 g. of clear liquid. Treatment with dry hydrogen chloride in ether afforded 1.0 g. of the hydrochloride of X (25% yield). A sample was recrystallized from methanol-ether.

*Anal.* Calcd. for $C_6F_4H_{10}NCl$ (207.6): C, 34.7; H, 4.85; Cl (ionic), 17.1. Found: C, 35.0; H, 4.64; Cl, 17.4.

**Acknowledgment.**—Miss Catharine Brown performed the elemental analyses reported here. Dr. John De Vries and Mr. William Anderson prepared and calibrated the n.m.r. spectra.

# The Preparation and Some Reactions of Trifluorovinyllithium[1]

PAUL TARRANT, PETER JOHNCOCK, AND JOHN SAVORY

*Department of Chemistry of the University of Florida, Gainesville, Florida*

*Received July 16, 1962*

Trifluorovinyllithium has been prepared by an exchange reaction with trifluorovinyl bromide and an alkyllithium reagent. Its reaction with some aldehydes and ketones are described. An investigation of the stability of trifluorovinyllithium has been carried out.

Several workers[2–7] have made use of trifluorovinylmagnesium halides in the synthesis of derivatives of Groups II, III, IV, and V elements, as shown below for the mercury compound.

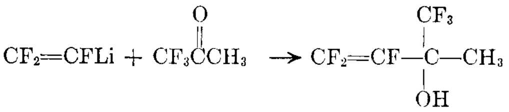
$$CF_2{=}CFMgI + HgCl_2 \longrightarrow (CF_2{=}CF)_2Hg$$

It thus seemed desirable to develop a practical method of synthesis of the corresponding lithium reagent and to study its properties.

Seyferth and co-workers[8] prepared trifluorovinyllithium by treating triphenyl(trifluorovinyl)tin with phenyllithium. Their primary objective was the determination of differences in the behavior of organometallic compounds and their synthesis of the lithium reagent is not a good preparative method.

Knunyants and his associates have reported[9] that trifluorovinyl iodide exchanged with phenylmagnesium bromide to give trifluorovinylmagnesium bromide and iodobenzene. Dixon,[10] however, reported that lithium reagents replaced fluorine atoms in a fluoroölefin. Therefore, it was of some interest to find that exchange rather than addition with loss of fluoride ion occurred when bromotrifluoroethylene reacted with methyl- or butyllithium. Yields of trifluorovinyllithium of at least 73% were realized.

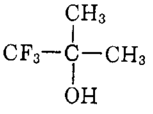
The extent of exchange was determined by reaction with trifluoroacetone to give the corresponding alcohol (I).



$$CF_2{=}CFLi + CF_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \rightarrow CF_2{=}CF{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CF_3}{|}}{C}}{-}CH_3$$

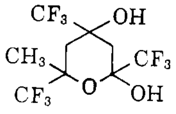
I

Side reactions gave small amounts of 2-trifluoromethyl-2-propanol (II) and a cyclic ether (III).



$$CF_3{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3$$

II



III

Compound III had been prepared previously[11] by reaction of trifluoroacetone with sodium. Compound II was obviously produced from the reaction of trifluoroacetone with methyllithium.

The alcohol (I) showed no tendency to rearrange under the reaction conditions employed, although previously workers[12] had found that similar compounds rearranged to α-fluoro-α,β-unsaturated acid fluorides.

This type of rearrangement has also been studied in our laboratories.[13] Here it was found that the presence

---

[1] Presented at the Second International Fluorine Symposium, Estes Park, Colo., July 17–20, 1962.

[2] I. L. Knunyants, R. N. Sterlin, R. D. Yatsenko, and L. N. Pinkina, *Chem. Abstr.*, **53**, 6987 (1959); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1345 (1958).

[3] H. D. Kaeze, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 6336 (1959).

[4] R. N. Sterlin, V. Li, and I. L. Knunyants, *Chem. Abstr.*, **54**, 1273 (1960); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1506 (1959).

[5] R. N. Sterlin, L. N. Pinkina, R. D. Yatsenko, and I. L. Knunyants, *Chem. Abstr.*, **54**, 14103 (1960); *Khim. Nauka i Promy.*, **4**, 800 (1959).

[6] R. N. Sterlin, I. L. Knunyants, L. N. Pinkina, and R. D. Yatsenko, *Chem. Abstr.*, **54**, 1270 (1960); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1492 (1959).

[7] R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, and I. L. Knunyants, *Chem. Abstr.*, **54**, 10838 (1960); *Khim. Nauka i Promy.*, **4**, 810 (1959).

[8] D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Letters*, No. **22**, 20 (1960).

[9] R. N. Sterlin, L. N. Pinkina, I. L. Knunyants, and L. F. Nezgovorov, *Khim. Nauka i Promy.*, **4**, 809 (1959); *Chem. Abstr.*, **54**, 10837 (1960).

[10] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

[11] A. L. Henne and P. E. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5148 (1954).

[12] R. N. Sterlin, R. D. Yatsenko, and I. L. Knunyants, *Khim. Nauka i Promy.*, **3**, 540 (1958); *Chem. Abstr.*, **53**, 4195 (1959).

[13] P. Tarrant and R. D. Richardson, Abstract of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p. 17-M.